Advanced Nanoporous Composite Materials for Industrial Heating Applications

Towards Low-Cost Nanostructured Refractories

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Industrial Needs for Nanostructured Refractory Materials

- Insulations:
  - Regenerators, ports, crowns, forebay channel, etc.
- Low thermal-conductivity Refractories
  - Useful in many areas of industry
    - Shorter heat-to-temperature times
    - Other process improvements to maximize throughput
- Desired performance improvements:
  - Lower thermal conductivity
  - Longer life times
  - Increased corrosion resistance
  - Lower cost

Aerogels: Background & Process

- Aerogels: Nanoporous, open-celled solids formed by controlled removal of the liquid phase from a gel.
  - First prepared by Samuel Kistler in 1931
- Typical preparation:
  - Sol-Gel formation of wet gel
    - Hydrolysis-condensation of Alkoxides
    - Organic polymerization
    - Other colloid-forming methods
  - Supercritical drying
    - Alcohol drying
    - CO_2 substitution-drying

Challenges for High Temperature Uses

- Must withstand temperatures of 700-1500 °C
  - Increase sintering resistance
- Must be chemically inert
- Must show reduced thermal conductivity
  - Targets: 0.01-0.10 W/m-K for ***Insulations***
  - <0.5 W/m-K for ***Refractories***
- Must be affordable
- Composition:

$x(Al_2O_3)\bullet y(Cr_2O_3)$ or $x(0.94Al_2O_3/0.06SiO_2)\bullet y(Cr_2O_3)$

Synthesis of Al_2O_3-Cr_2O_3 Aerogels

- Sol-Gel preparation via Acid-Base/Redox reactions

$$xAl(OH)_3 \quad + \quad yCrO_3 \xrightarrow[x\ HNO_3]{H_2O} xAl^{3+} \bullet yCrO_4^{2-} \bullet xNO_3^{-}$$

(aqueous
)

$$xAl^{3+} \bullet yCrO_4^{2-} \bullet xNO_3^{-} \xrightarrow[s.c.\ CO_2]{\text{ethanol}} xAl(OH)_2NO_3 \bullet yCrO_2$$

(solid aerogel)

$$xAl(OH)_2NO_3 \bullet yCrO_2 \xrightarrow{1000\ ^\circ C} xAl_2O_3 \bullet yCr_2O_3$$

(nanostructured
powder)

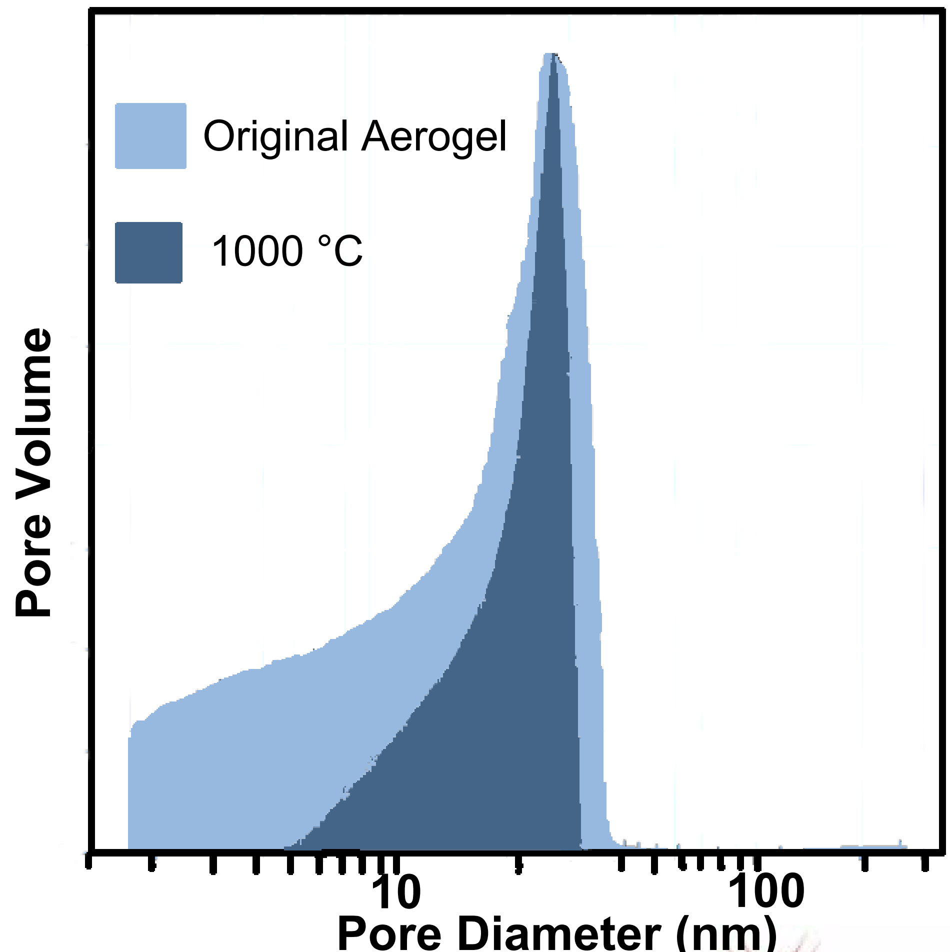
Effect of Temperature on Surface Area

- Surface areas (BET) of various compositions before and after firing (m^2/g)

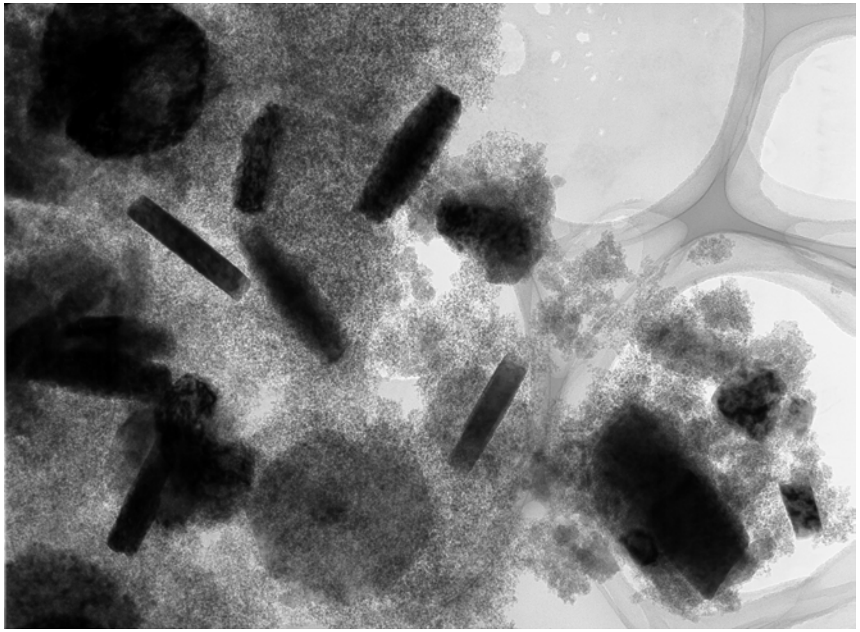
Compound	Neat aerogel	450 °C	1000 °C
Cr_2O_3	290	13	13
$Al_2O_3 \cdot 2Cr_2O_3$	270	180	41
$Al_2O_3 \cdot Cr_2O_3$	260	160	44
$2Al_2O_3 \cdot Cr_2O_3$	240	170	64
$2(0.94Al_2O_3 \cdot 0.06SiO_2) \cdot Cr_2O_3$	350	----	130

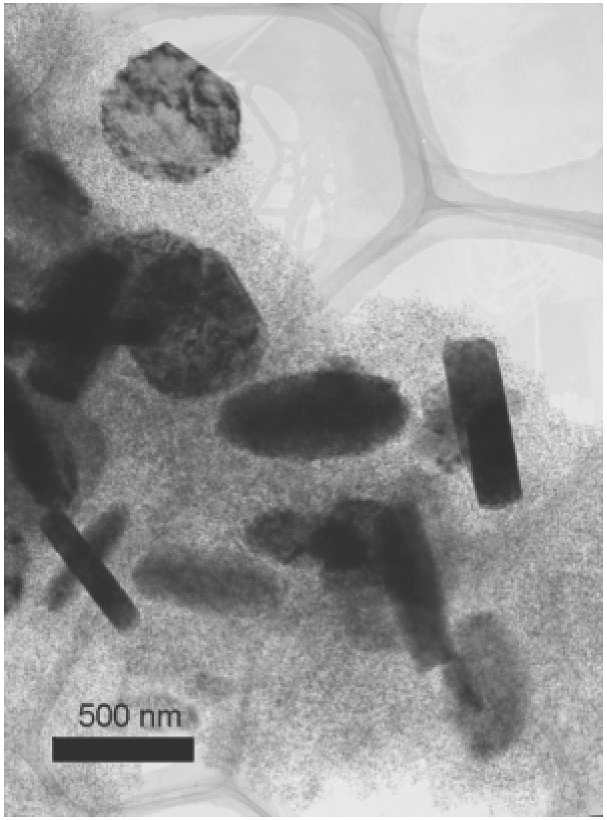
Porosity After Thermal Processing

- Peak of Pore size distribution is ~ 26 nm
- Considerable pore volume between 2-10 nm
- Thermal treatment closes smaller pores
- Peak remains at ~26 nm



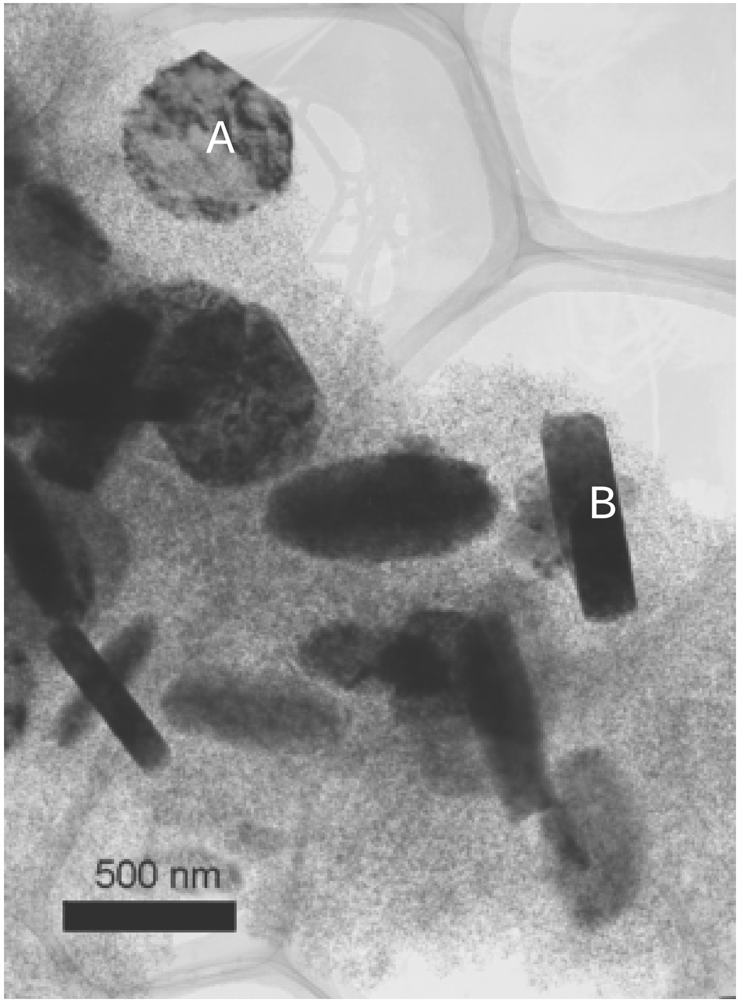
TEM Images of Al_2O_3-Cr_2O_3 Aerogels

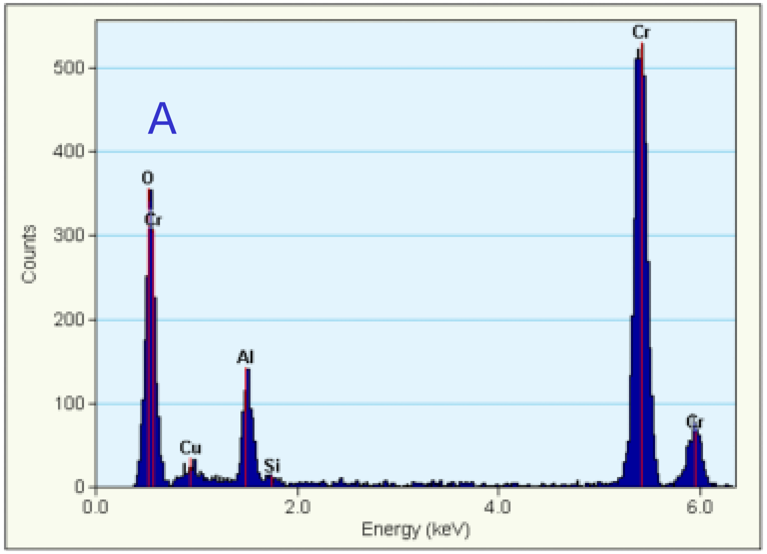


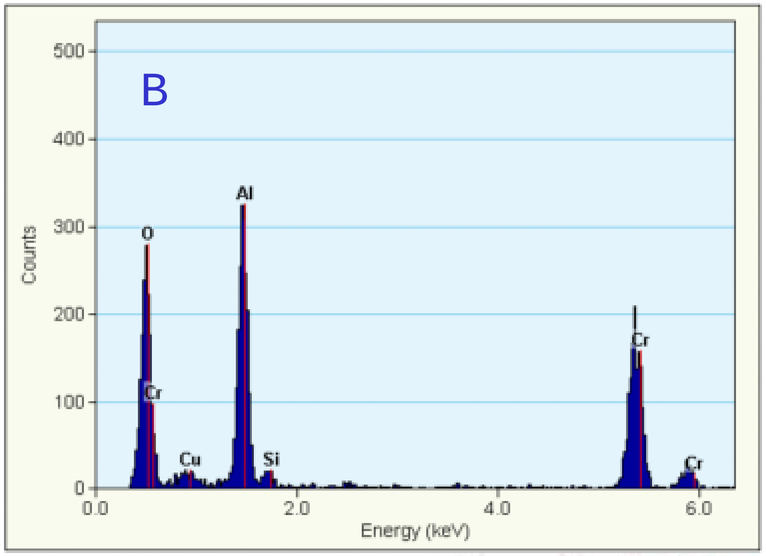


Acid- Base route

EDX Indicates Two Phases

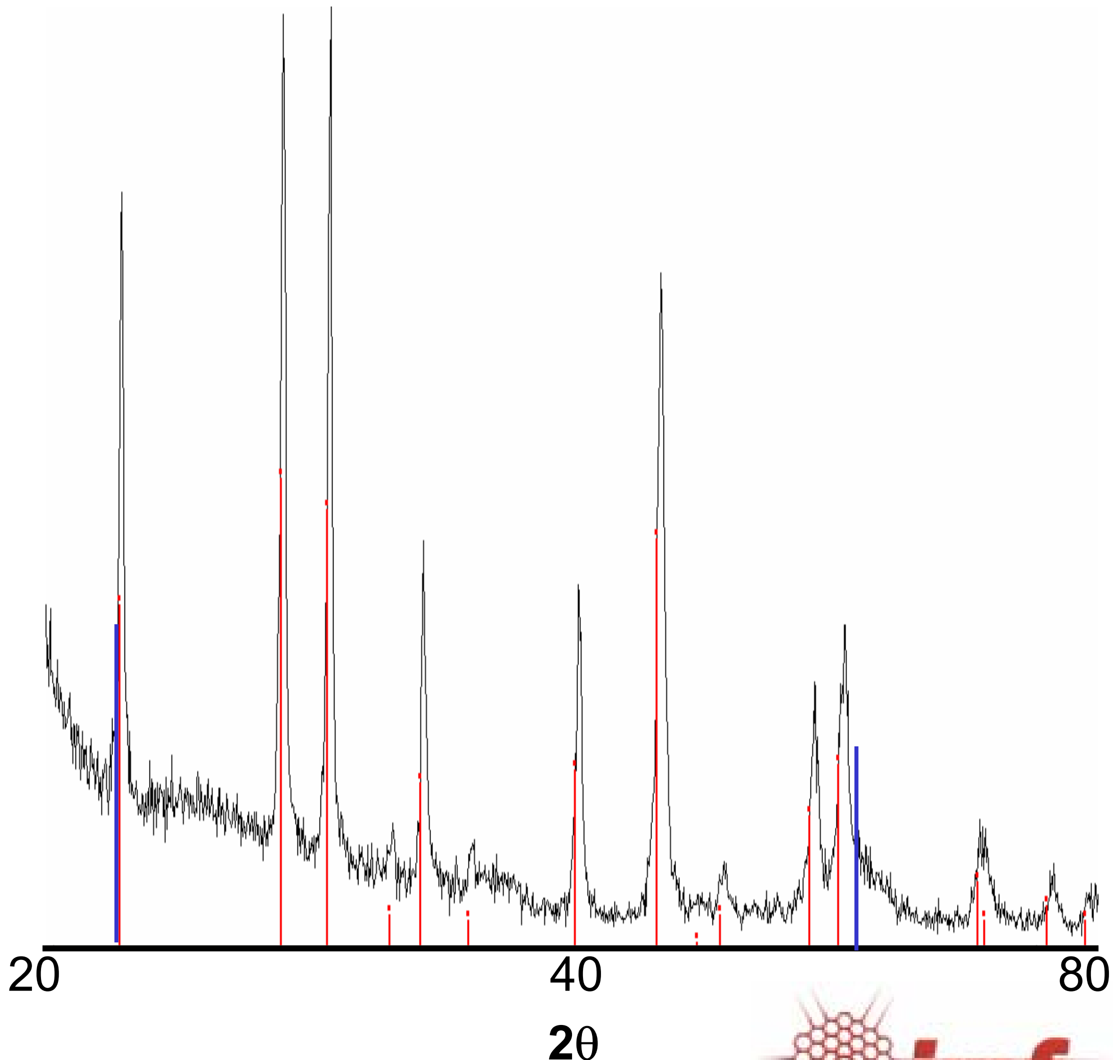






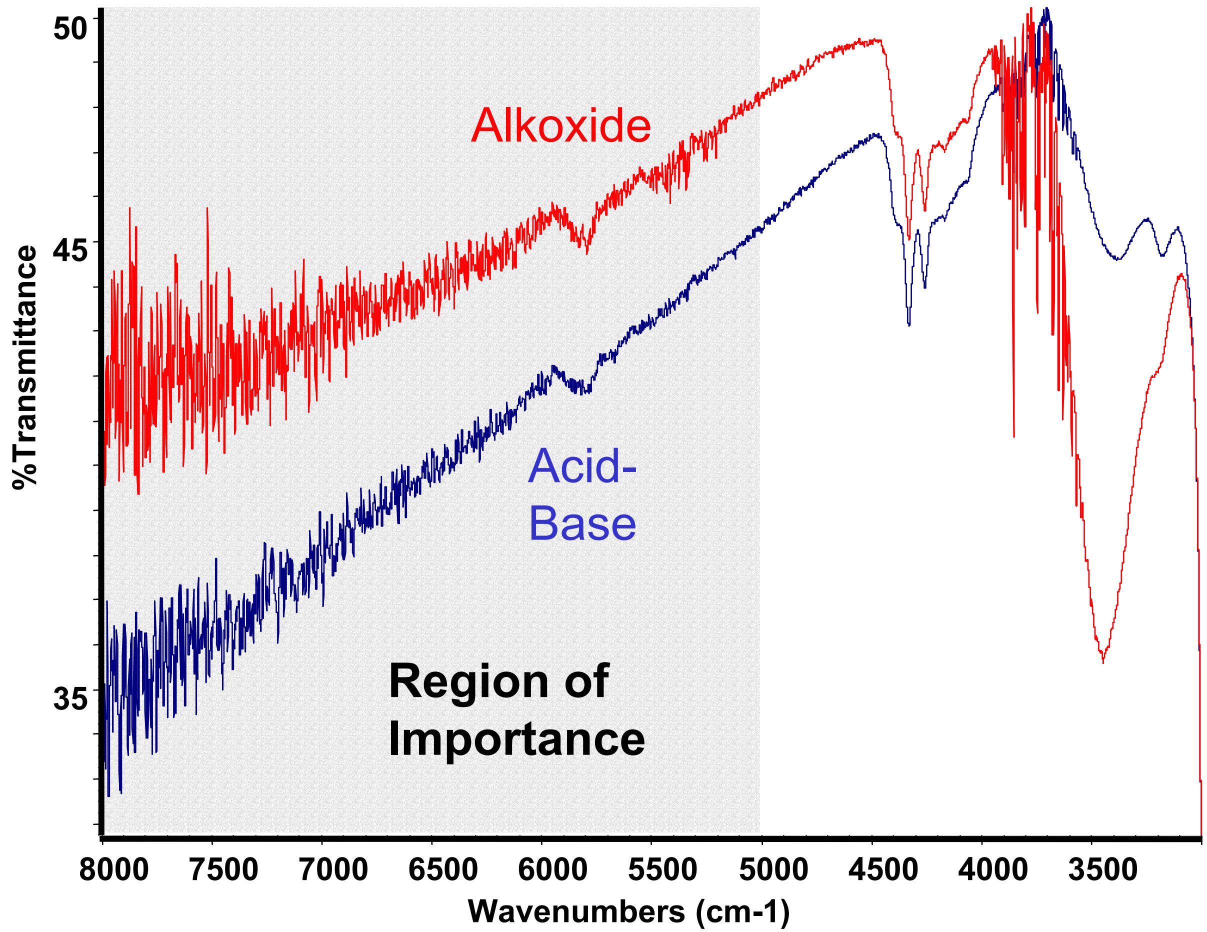
X-Ray Identification

- Acid-base derived aerogel shows one primary crystalline phase:
  - Eskolaite, Cr_2O_3
- Second phase may also be present;
  - $Al_{1.4}Si_{0.3}O_{2.7}$



Opacity of Al-Cr Aerogels

- 0.1-1.5 micron crystal inclusions scatter incident IR radiation
- Firing leads to a high # density of crystals
- Shows lower transmittance in area of interest
- Material is largely self-opacified



Thermal Conductivity

- Samples of Al_2O_3-Cr_2O_3 aerogel evaluated using the laser flash method at ORNL (MPLUS Program)
  - Low (100-300 °C) temperature thermal conductivity: ~0.15 W/m-k
  - 10X-20X lower than standard Cr- and Al-based refractory blocks
  - High temperature testing underway

Low-Cost Raw Materials

- Precursors to Al_2O_3-Cr_2O_3 aerogels are very affordable
  - 81¢ per pound of product vs. $64/lb for traditional alkoxide precursors

- Other compositions derived from near-mineral precursors to be investigated

Target Application for Al_2O_3-Cr_2O_3 Aerogel

- Originally planned as a backing insulation material
  - Difficult (but possible) to compete with current silica-based products
- IHEA Materials Forum (ORNL Feb '03) revealed a greater need for low thermal conductivity refractories
  - Use this material as an additive to lower the heat loss of current refractories
  - Industrial collaborations planned

Future Work

- Continue characterization of alumina-chromia aerogels
- Begin testing this material as a component of various composite refractory blocks to lower their thermal conductivity
  - Industrial collaborations
- Expand program to look at various other routes to nanostructured materials derived from commodity raw materials
- Develop new “one-pot” synthesis and processing method
  - Greatly increase production throughput.
  - Additional cost savings
- Combine new process with low-cost raw materials
  - Dramatic drop in product cost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